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CORROSION AND CORROSION RESEARCH

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CORROSION AND CORROSION RESEARCH

Thomas R. Camp,¹ M. ASCE

SYNOPSIS

The paper describes the elements of the corrosion cell and demonstrates that a great variety of half-cell reactions are possible whose single electrode potentials may be computed from thermodynamic constants and the composition of the water. It is demonstrated that only those half-cell reactions which produce the greatest electromotive force can take place. The method of identification of the half-cell reactions for a particular case is illustrated. It is shown that the theory may be used to great advantage in selecting water treatment processes for corrosion control. The theory underlying the correct procedure for polarization tests is developed, and it is shown that all unknowns may be evaluated if the single electrode potentials are computed first.

INTRODUCTION

The corrosion of a metal consists of the solution of the metal in water or in an aqueous solution with which it is in contact, or the reaction of the solid metal with ions and other dissolved constituents of the solution. Either reaction is an oxidizing reaction accompanied by the release of electrons which flow back through the metal as a negative electric current. Since the water or aqueous solution is a part of the electric circuit, the complete circuit is an electric cell including the anode at which the corrosion is taking place, a cathode which is connected to the anode by the metal as a conductor and at which a reducing reaction takes place, and the electrolyte between the anode and cathode.

The basic theory underlying the electrochemical process of corrosion of metals in contact with water was first developed by Josiah Willard Gibbs about 1875-78. Gibbs' great contributions to electrochemistry were not used to any considerable extent in this country until after the publication by Lewis and Randall in 1923 of their book, "Thermodynamics and Free Energy." Since 1923 a great mass of experimental data has been collected relating to free energies of chemical substances and single electrode potentials, much of which has been used in the evaluation of equilibrium constants. Unfortunately, very little of this very useful information has been applied to the development of the electrochemical theory of corrosion. Because of the economic importance of corrosion, there has been a vast amount of research activity; but most of it has been directed towards tests of the relative merits of various metals and their alloys, of various protective coatings and of cathodic protection. Very little attention has been paid to the half-cell reactions

1. Camp, Dressler & McKee, Consulting Engineers, Boston, Mass.

which take place during the corrosion process and to the complete electric circuit.

As a step towards filling this vacuum in our knowledge of corrosion, the author published two papers on "Corrosiveness of Water to Metals"² in 1946. In these papers much of the basic theory relating to the equilibria of corrosion reactions was presented, and it was shown that the half-cell reactions which actually take place in a corrosion process can be identified from the analysis of the water and the comparison of the single electrode potentials of the possible reactions.

The principles presented in these two papers have been extremely useful to the author in explaining what takes place during various corrosion phenomena, and in evaluating protective coatings and corrective water treatment processes. The application of these principles indicates that some of the reactions which are said to take place in the conventional corrosion literature do not take place under normal conditions, and that a host of other half-cell reactions which are uniformly neglected in corrosion literature actually can and do take place. Since the rate of corrosion depends upon the potentials of the half-cell reactions and the resistances in the electric circuit, it should be obvious that any worth-while fundamental research on rates of corrosion should start with the identification of the electrochemical reactions which are taking place and the evaluation of the resistances in the circuit.

During the years since the publication of the above-referred to papers by the author, the principles presented have been used very little by others. The purpose of this paper is to present again in brief and simplified form the essentials of the previous papers together with proof of their validity and a development of the theory of the electric circuit in the corrosion process in the hope that the principles involved will be better understood and more widely used in corrosion laboratories and by corrosion consultants. Examples of the application of the principles are also presented to illustrate the procedures and the results which may be obtained.

Elements of the Corrosion Cell

In order for corrosion to take place there must be moisture in contact with the metal and the moisture must contain ions to form the electrolyte. There must be anodic areas at which the anodic half-cell reactions or oxidations take place and there must be cathodic areas at which the cathodic half-cell reactions or reductions take place. The anode and the cathode of an elementary corrosion cell must be connected by an electrical conductor, usually the metal undergoing corrosion, but also in many cases including the films or coatings over the metal surface. In the initial stages of the common form of corrosion the anode and cathode are very close together, for the principle of least action requires that the path of current flow and the resistance be the least. Therefore, in normal corrosion the anode may be only a few molecules removed from the cathode, so close, in fact, that the casual observer will overlook the fact that two separate electrochemical reactions are taking place.

Fig. 1 shows a metal in contact with water with several different types of half-cell corrosion reactions taking place. The scale of the drawings is large enough to indicate the anode and cathode as completely separated in space as they are in fact. At the anodic reaction, electrons are released by the corroding metal, which flow back through the metal and the films to the cathode

2. Journal of the New England Water Works Association, Vol. LX No. 2 & No. 3.

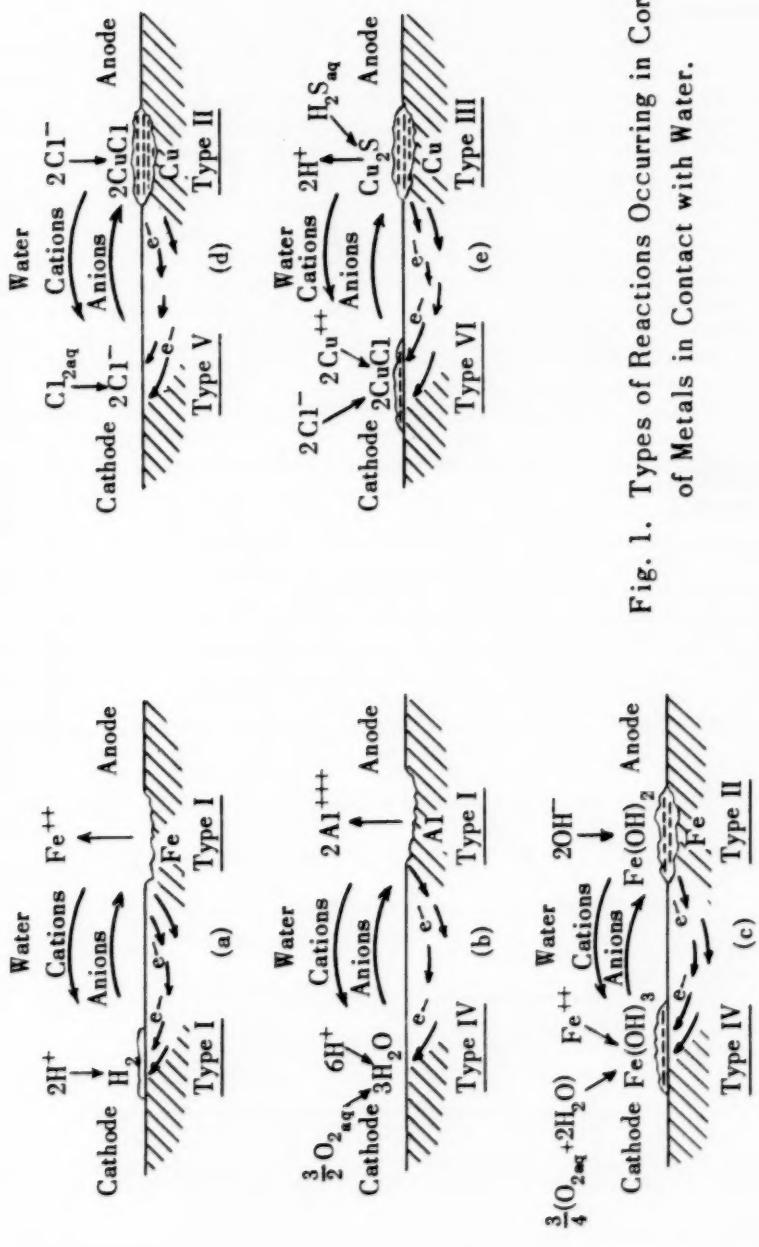


Fig. 1. Types of Reactions Occurring in Corrosion of Metals in Contact with Water.

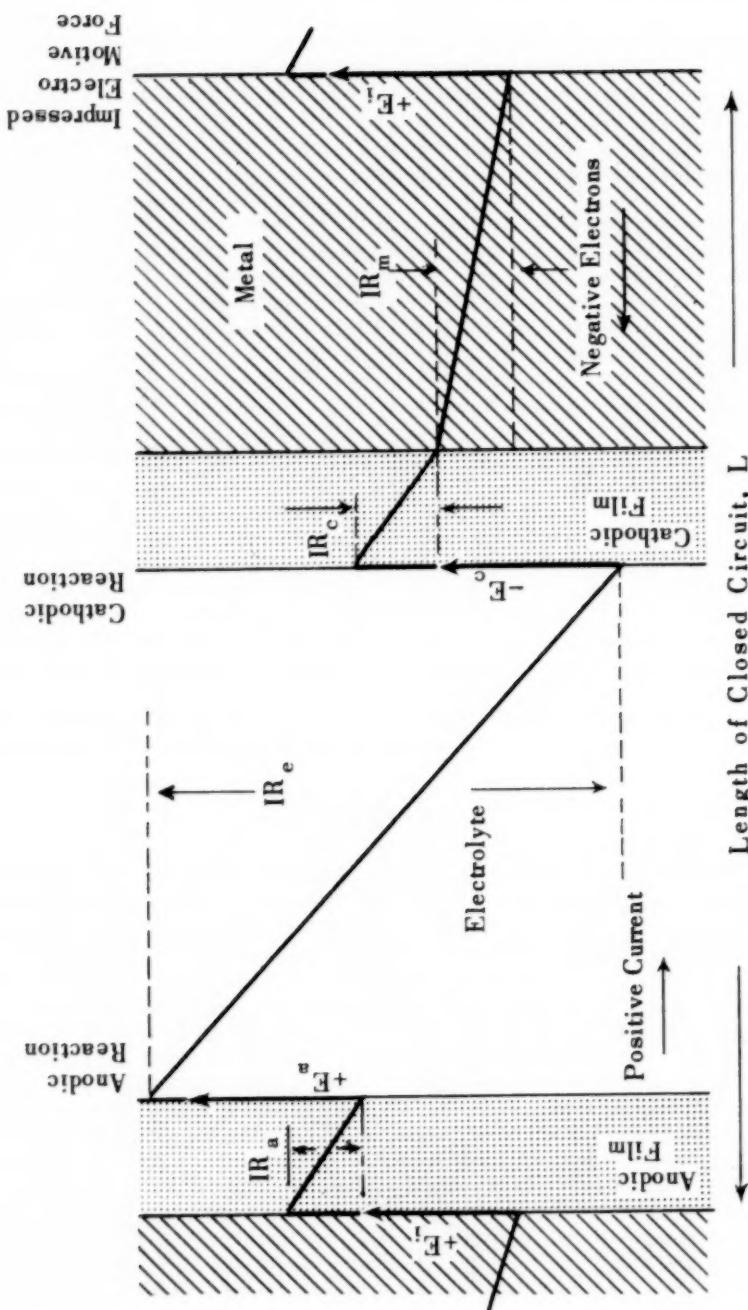


Fig. 2. Potential Profile around Corrosion Circuit.

where they are captured in the cathodic reaction. The so-called positive electric current flows through the electrolyte from the anode to the cathode.

It will be noted in Fig. 1 that several different types of anodic reactions other than the solution of the metal may take place. The reactions shown in Fig. 1 (a) are those which are said to take place by conventional theory in the corrosion of iron. A study of the principles indicates that at high pH values the anodic reaction shown in Fig. 1 (c) may take place, or carbonate and bi-carbonate ions may plate out at the anode to form ferrous carbonate. A study of the principles also indicates that plating out of hydrogen ions at the cathode as shown in Fig. 1 (a) does not take place except at very low pH values. A study of the principles also shows that the formation of water at the cathode takes place as shown in Fig. 1 (b) rather than by means of the plating out of molecular hydrogen and its subsequent reaction with dissolved oxygen as claimed in the conventional literature. The chemical combination of hydrogen and oxygen to form water, in the absence of an electric cell, occurs only at high temperatures. A study of the principles also shows that ferric iron rust is formed as shown in Fig. 1 (c) which reaction will prevail instead of the cathodic reaction involving the formation of water if there is a measurable amount of ferrous iron in solution. The claim in conventional literature that ferric iron rust is formed by a chemical reaction not a part of the electrochemical cell does not explain why the rust is nearly always attached to the corroding metal.

In accordance with Kirchhoff's second law, the electromotive force of the corrosion cell must equal the voltage drop caused by the resistance around the corrosion circuit. The potential or voltage profile around the corrosion circuit is illustrated diagrammatically in Fig. 2. The circuit illustrated in Fig. 2 includes an impressed electromotive force such as might be used in a test cell studying corrosion. The direction shown for the impressed electromotive force is such as to increase the current I, but it should be noted that the current might be reduced to zero or reversed by an electromotive force of sufficient magnitude in the opposite direction. The circuit also includes in the interest of completeness an anodic film or coating and a cathodic film or coating. In accordance with Kirchhoff's second law, the following relations hold:

$$E_i + E_a - E_c = I(R_a + R_e + R_c + R_m) \quad (1)$$

where E_i = the impressed electromotive force,

E_a = the single electrode potential at the anode,

E_c = the single electrode potential at the cathode,

I = the corrosion current,

R_a = the resistance of the anodic film or coating,

R_e = the resistance of the electrolyte,

R_c = the resistance of the cathodic film or coating,

and R_m = the resistance of the metal.

For a clear understanding of the corrosion process, one must keep in mind that there are two separate regions in a corrosion cell where electrochemical half-cell reactions take place and that the reactions at the anode are completely independent of the reactions at the cathode, except that no current can flow without two half-cell reactions. Moreover, the electromotive force at the anode and the electromotive force at the cathode are completely independent of the rate of current flow despite opinions expressed to the contrary in current literature.³ The potentials of the half-cell reactions depend only upon the temperature, the participating substances and the activities of the participating substances as shown hereinafter in Equations (2), (3), and (4).

The circuit shown in Fig. 2 is of course idealized to indicate complete separation of anode and cathode and a single length for the path of flow of the electric current. The actual corrosion cell is, of course, very much more complicated with numerous stream paths of different length for current flow and variable thicknesses of films. In order to study the process, however, it is essential to separate the variables, and this can only be done in the laboratory by means of an experimental corrosion cell in which all factors are measurable and controllable. Fig. 2 represents such an idealized circuit.

The rate of corrosion is the time rate at which the reactions at the anode take place. The rate is the same at the cathode and throughout the corrosion circuit, and is measured by the corrosion current. In accordance with Faraday's law, the corrosion current in amperes is equal to 96,500 times the number of equivalents per second taking part in the anodic reactions or in the cathodic reactions. For example, for a corrosion rate of 0.01 inches per year for iron, the corrosion current is approximately 2.16×10^{-5} amperes per square centimeter of iron surface; provided, however, that ferrous iron is participating in all of the reactions at the anode.

An examination of Equation (1) or Fig. 2 will indicate that for a given total electromotive force the corrosion current, and hence the rate of corrosion depends upon the resistance of the corrosion circuit. In fundamental corrosion research, therefore, it is most important to know the resistances of the elements of the corrosion circuit. The resistance of the electrolyte may be computed from its equivalent conductance, and the resistance of the metals and films may be computed from the specific resistance of the substances if the lengths are known. Unfortunately there is very little information in the literature relative to the specific resistance of the films encountered in the corrosion process. This is one of the fertile fields for future research.

Principles for the Identification of Half-cell Reactions

The reactions at the electrodes of a corrosion cell will depend upon the metals and upon the kind and concentration of ions and other solutes adjacent to the electrodes. Of all possible anodic reactions, the reaction or reactions with the highest potential will prevail, and of all possible cathodic reactions the ones with the lowest potential will prevail. Thus at any instant the reactions will be those which produce the greatest electromotive force for the cell. At any instant there is a single electromotive force corresponding to the half-cell reactions at each electrode. If two or more half-cell reactions are occurring simultaneously at a point in an electrode, therefore, the

3. J. M. Pearson, Trans. The Electrochemical Society, Vol. 81, 1942, p 489; Uhlig, H. H., "Corrosion Handbook," Wiley, 1948, p. 483; and Eliassen and Lamb, J.A.W.W.A., Vol. 45, 1953, p. 1290.

concentrations of the reactants must be such as to produce the same electromotive force. The above-stated principle is the basis for the identification of the corrosion reactions, and it is the only contribution of the author's 1946 papers which appears to be new. Since it has not been generally accepted, arguments in support of the validity of the principle are presented below.

As is well known, the electromotive series of the metals is a table of standard single electrode potentials arranged in order of magnitude of the electromotive forces with those of greatest magnitude at the top. As is also well known, if any two of the metals are immersed as electrodes in an aqueous solution containing molal concentrations of the metals, the metal highest in the series will enter solution and the other will plate out. The electromotive force of the cell will be the difference of the standard single electrode potentials. If the concentrations of the ions of the two metals is different from the molal concentrations, the single electrode potentials will differ from the standard potentials; but the metal with the highest potential will be the anode, and the electromotive force of the cell will be the difference of the actual potentials.

The single electrode reactions of the metals are only special cases of the more general type of half-cell reaction which must be considered in corrosion phenomena. The same laws govern in all cases, and, if only two half-cell reactions are possible in a corrosion cell, the one with the highest potential will be the anodic reaction. If more than two half-cell reactions are possible, it is easy to see that the direction of flow of positive current will be from the reactions of higher potential to those of lower potential; but it is not so obvious which of the reactions will prevail at anode and cathode.

Consider a single current streamline in a corrosion cell, as shown in Fig. 3, with the anodic reactions occurring at point A and the cathodic reactions at point C. For the corrosion current, I, at any instant, it is obvious that there can be only one value of the IR drop through the electrolyte, metal and films because there is only one value of the total resistance along the current streamline. Since the total IR drop is equal to the difference in electromotive force of the half-cell reactions, this difference also has only one value. Since the IR drop through the electrolyte along the current streamline has only one value, each of the half-cells has only one value for its potential. Two or more half-cell reactions may occur simultaneously at either electrode, but only if their potentials are equal.

Now which of the possible half-cell reactions do occur at the anode, those with the highest, those with the lowest, or those with intermediate potentials? Applying what we already know, the reactions with the highest potential will be anodic to those with the lower potentials and will prevail at the anode. The possible reactions at the anode with the lower potentials tend to be cathodic to the anodic reactions which prevail, but they are anodic to the prevailing reactions at the cathode. These reactions cannot take place, therefore, because they would proceed in both directions at the same time and would result in a flow of current in both directions through the same point in the metal interface at the same time. Moreover, they would result in more than one value for the total IR drop. Similar reasoning will show that of all possible cathodic reactions, the ones with the lowest potential will prevail and all others will be inactive.

Referring again to Fig. 3, it is evident that all parallel current streamlines in the corrosion circuit must follow the same laws. Therefore, at all points in the anodic area, the half-cell reactions with the highest potential will prevail; and at all points in the cathodic area, the reactions with the lowest

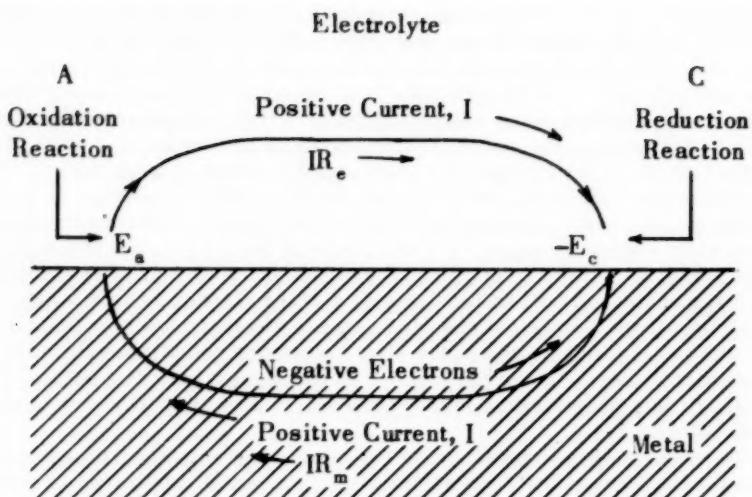


Fig. 3. Current Streamline in Corrosion Cell.

potential will prevail. All other possible reactions will be inactive.

From the above discussion it follows that the half-cell reactions which actually are taking place in a corrosion cell may be identified by comparing all possible reactions until those are found which produce the highest electromotive force for the cell. The conclusions previously drawn relative to the half-cell reactions illustrated in Fig. 1 were arrived at by this procedure.

In order to determine the electromotive force of a half-cell reaction, it is necessary to have available or to determine the so-called standard electrode potential of the reaction which is based upon an activity of unity for each of the reacting substances and to modify this potential to conform with the actual concentrations of the reacting substances. The standard electrode potentials may be computed from the free energies of formation of the reacting substances. The free energies of a large number of substances are available for the standard temperature of 25°C .⁴

In writing half-cell reactions it is conventional to write them in the oxidation direction proceeding from left to right, and the potentials are computed in the same direction. When a reaction becomes cathodic, the direction is reversed and the potential changes sign. The standard oxidation potential of any half-cell reaction at any temperature T may be computed from the standard free energy change at the same temperature as follows: ((2) on next page)

The actual oxidation potential of a half-cell reaction at temperature T may be computed from the standard oxidation potential and the activities of the participating substances as follows: ((3) on next page)

4. "Oxidation Potentials" by Latimer, Prentice-Hall, 1938.

$$E_T^\circ = - \frac{4.183}{96500 n} \Delta F_T^\circ \quad (2)$$

where E_T° = the standard oxidation potential referred to the hydrogen electrode,

n = the number of electrons transferred per mole,

4.183 = the number of joules per calorie,

96500 = the number of coulombs per faraday,

and $-\Delta F_T^\circ$ = the decrease in free energy of the half-cell reaction in calories per mole.

$$E_T = E_T^\circ - \frac{4.183 \times 2.302 RT}{96500 n} \log Q$$

$$\text{or } E_T = E_T^\circ - \frac{1.978 \times 10^{-4} T}{n} \log Q \quad (3)$$

where E_T = the oxidation potential at absolute temperature T ,

T = the absolute temperature in $^{\circ}\text{K}$
($T = 298^{\circ}\text{K}$ for 25°C),

R = the gas constant = 1.985 calories per mole per $^{\circ}\text{K}$,

and Q = the ratio of the product of the activities of the products of the reaction to the product of the activities of the reactants.

At the temperature of 25°C (298°K), Equation (3) reduces to the following:

$$E_{25} = E_{25}^{\circ} - \frac{0.05914}{n} \log Q \quad (4)$$

where E_{25} = the oxidation potential at 25°C.

and E_{25}° = the standard oxidation potential
at 25°C.

Since most of the thermodynamic constants on free energy, standard potentials, entropies and heats of reactions have been referred to a temperature of 25°C and are available in tables, it is convenient to start all computations for this temperature and then adjust to the actual temperature T. For the temperature adjustment, the Gibbs-Helmholtz equation⁵ may be used. This equation, in a form most convenient for our use, is as follows:

$$E_T^{\circ} = E_{25}^{\circ} + \frac{T - 298}{T_{av}} \left(E_{25}^{\circ} + \frac{\Delta H_{25}^{\circ}}{23066 n} \right) \quad (5)$$

$$\text{where } T_{av} = \frac{298^{\circ}\text{K} + T}{2}$$

and ΔH_{25}° = the heat of the reaction at 25°C.

If the heat of the reaction, ΔH_{25}° , is not available, it may be computed from the free energy and entropy by means of the following equation:

$$\Delta H_{25}^{\circ} = \Delta F_{25}^{\circ} + 298 \Delta S_{25}^{\circ} \quad (6)$$

where ΔS_{25}° = the change in entropy of the reaction
at 25°C.

Application of Theory to Identify Half-cell Reactions

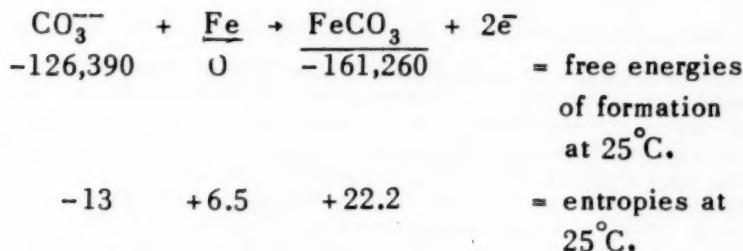
In order to illustrate the application of the above equations, consider the following example:

5. MacInnes, D. A., "The Principles of Electrochemistry," Reinhold, 1939,
p. 110.

Example 1

Compute the oxidation potential of the following reaction at 10°C, if the carbonate ion concentration is 2.5 ppm.

Solution:



$$\Delta F_{25}^\circ = -161,260 + 126,390 = -34,870 \text{ calories}$$

$$E_{25}^\circ = -\frac{4.183}{96500 \times 2} (-34,870) = +0.755 \text{ volts}$$

$$\Delta S_{25}^\circ = +22.2 + 13 - 6.5 = +28.7$$

$$\Delta H_{25}^\circ = -34,870 + 298 \times 28.7 = -26,310 \text{ calories}$$

$$E_{10}^\circ = +0.755 + \frac{-15}{290.5} \left(+0.755 + \frac{-26,310}{23066 \times 2} \right)$$
$$= +0.745 \text{ volts}$$

For 2.5 ppm of CO_3^{--} , the molal concentration

$$[\text{CO}_3^{--}] = \frac{2.5}{60} \times 10^{-3} = 4.167 \times 10^{-5}$$

For the dilute concentrations usually encountered in water works practice, the activity of an ion may be taken as equal to its concentration without appreciable error.

Then for 10°C or $T = 283$,

$$E_{10} = +0.745 - \frac{1.978 \times 10^{-4} \times 283}{2} \log\left(\frac{1}{4.167 \times 10^{-5}}\right)$$
$$= +0.684 \text{ volts}$$

The standard oxidation potentials at 25°C , E_{25}° , are available for numerous half-cell reactions and do not need to be computed as illustrated above.⁶

The procedure to be used in identifying the half-cell reactions for a particular case will be illustrated in the following example for a soft water at high pH in contact with iron. This water is typical of soft New England waters following pH adjustment with sodium hydroxide. The analysis of the water has been assumed so that Fe(OH)_2 , CaCO_3 , Ca(OH)_2 , and Mg(OH)_2 are below saturation. There is a slight supersaturation of FeCO_3 and MgCO_3 such that some precipitation might occur of these compounds by ordinary chemical reactions. For simplicity the temperature has been taken at 25°C .

Example 2.

Determine the anodic and cathodic reactions for the corrosion of an iron pipe in contact with water at 25°C , the water having a pH of 9.5 and containing 4 ppm of calcium, 1.0 ppm of magnesium, 0.06 ppm of ferrous iron, 2.5 ppm of carbonate, 17.1 ppm of bicarbonate and 6.4 ppm of dissolved oxygen.

Solution:

The concentrations of the reacting substances are as follows:

$$[\text{H}^+] = 10^{-9.5} = 3.16 \times 10^{-10}$$

$$[\text{OH}^-] = 10^{-4.5} = 3.16 \times 10^{-5}$$

$$[\text{Ca}^{++}] = \frac{4}{40} \times 10^{-3} = 10^{-4}$$

$$[\text{Mg}^{++}] = \frac{1}{24.3} \times 10^{-3} = 4.12 \times 10^{-5}$$

$$[\text{Fe}^{++}] = \frac{0.06}{55.8} \times 10^{-3} = 1.074 \times 10^{-6}$$

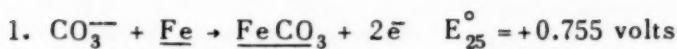
$$[\text{CO}_3^{--}] = \frac{2.5}{60} \times 10^{-3} = 4.167 \times 10^{-5}$$

$$[\text{HCO}_3^-] = \frac{17.1}{61} \times 10^{-3} = 2.81 \times 10^{-4}$$

$$[\text{O}_{2\text{aq}}] = \frac{6.4}{32} \times 10^{-3} = 2 \times 10^{-4}$$

6. Latimer, "Oxidation Potentials," and the author's 1946 papers.

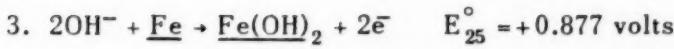
Consider the following possible reactions which have been arranged in order of decreasing potential:



$$E_{25} = +0.755 - \frac{0.05914}{2} \log \left(\frac{1}{4.167 \times 10^{-5}} \right) = +0.625 \text{ volts}$$



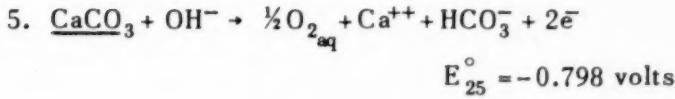
$$E_{25} = +0.44 - \frac{0.05914}{2} \log (1.074 \times 10^{-6}) = +0.616 \text{ volts}$$



$$E_{25} = +0.877 - \frac{0.05914}{2} \log \left[\frac{1}{(10^{-4.5})^2} \right] = +0.611 \text{ volts}$$

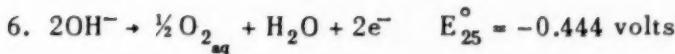


$$E_{25} = 0.0 - \frac{0.05914}{2} \log [(10^{-9.5})^2] = +0.561 \text{ volts}$$

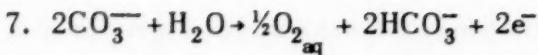


$$E_{25} = -0.798 - \frac{0.05914}{2} \log \left[\frac{(2 \times 10^{-4})^{\frac{1}{2}} (10^{-4}) (2.81 \times 10^{-4})}{3.16 \times 10^{-5}} \right]$$

$$= -0.653 \text{ volts}$$

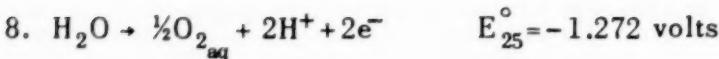


$$E_{25} = -0.444 - \frac{0.05914}{2} \log \left[\frac{(2 \times 10^{-4})^{\frac{1}{2}}}{(10^{-4.5})^2} \right] = -0.655 \text{ volts}$$

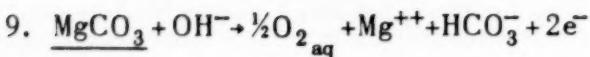


$$E_{25}^\circ = -0.661 \text{ volts}$$

$$E_{25} = -0.661 - \frac{0.05914}{2} \log \left[\frac{(2 \times 10^{-4})^{\frac{1}{2}} (2.81 \times 10^{-4})^2}{(4.167 \times 10^{-5})^2} \right]$$
$$= -0.655 \text{ volts}$$

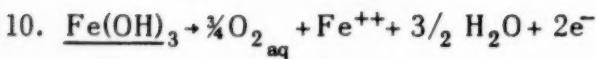


$$E_{25} = -1.272 - \frac{0.05914}{2} \log \left[(10^{-9.5})^2 (2 \times 10^{-4})^{\frac{1}{2}} \right]$$
$$= -0.655 \text{ volts}$$



$$E_{25}^\circ = -0.822 \text{ volts}$$

$$E_{25} = -0.822 - \frac{0.05914}{2} \log \left[\frac{(2 \times 10^{-4})^{\frac{1}{2}} (4.12 \times 10^{-5})(2.81 \times 10^{-4})}{3.16 \times 10^{-5}} \right]$$
$$= -0.665 \text{ volts}$$



$$E_{25}^\circ = -1.386 \text{ volts}$$

$$E_{25} = -1.386 - \frac{0.05914}{2} \log \left[(1.074 \times 10^{-6})(2 \times 10^{-4})^{\frac{3}{2}} \right]$$

$$= -1.126 \text{ volts}$$

The above reactions are not all the possible reactions which can take place, but others examined appear not to be important. Now if there is no film on the iron, it is evident that reaction (1), the plating out of carbonate at the anode will prevail at the start of the process and reaction (10) the formation of ferric iron oxide will prevail at the cathode.

A study of the reactions and potentials of Example 2 leads to many interesting conclusions. In the first place, the plating out of carbonate at the anode can continue only until all the exposed metallic iron has reacted with carbonate to produce a ferrous carbonate film one molecule deep. Thereafter the metal is no longer exposed to the reaction or to reactions (2) or (3). Corrosion as defined must therefore cease. Current may continue to flow in the corrosion cell, however, with other reactions with lower potential becoming anodic. Next in order is reaction (4) the formation of hydrogen ions from molecular hydrogen. Since no molecular hydrogen is available, reaction (4) can proceed only in the reverse direction and is inactive at the anode. Next in order as an anodic reaction is (5), but since no solid calcium carbonate is available, this reaction is inoperative. Reactions (6), (7) and (8) will prevail concurrently at the anode and if allowed to continue so as to change the composition of the water will lower the pH in the anodic areas.

Now let us consider what takes place at the cathode. In the example, the iron concentration is assumed to be 0.06 ppm. Since no iron is derived from the wall of the pipe, the iron must be a constituent of the water in the pipe. If the dissolved iron and oxygen are continuously replenished from the supply, ferric iron rust will continue to plate out at the cathode as indicated by reaction (10). If the iron is not replenished from the supply, as could be the case with a dead end pipe, the ferrous iron will be reduced in concentration by reaction (10) until the potential is increased to that of reaction (9). Thereafter magnesium carbonate will plate out along with iron rust until the electromotive force of the cell is reduced to zero and the current flow ceases.

It is of interest to note that in the absence of soluble ferrous iron, magnesium carbonate will plate out at the cathode, in the above example, by means of a half-cell electrochemical reaction involving dissolved oxygen. This reaction has been encountered in the author's experience in a case where magnesium carbonate crystals were found at cathodic areas on the exterior of a steel pipe which had been subjected to stray-current electrolysis. It may be shown that $MgCO_3$ plates out in preference to $CaCO_3$ at $25^{\circ}C$ unless the concentration of calcium is more than 6.5 times the magnesium concentration.

Most of the reactions in Example 2 are not to be found in the literature, and the reader will want experimental proof that they actually take place. Some recently reported experiments by Larson and King⁷ furnish confirmatory evidence to this end on some of the reactions. An experimental corrosion cell was devised with iron electrodes and nine compartments between the electrodes separated by porous Alundum plates. Tap water with a pH of 7.4, a hardness of 250 ppm and an alkalinity of 330 ppm was used for the electrolyte, and was allowed to flow continuously through the middle compartment. The water had a trace of iron and manganese, 60 ppm of calcium, 24 ppm of magnesium and 6.0 ppm of dissolved oxygen. Current was allowed to flow through the cell in one direction with an impressed electromotive force. The objective was to study ion migration.

Progressive quality changes occurred in each compartment with continuation of current flow. In the cathode compartment, the pH rose to 11, the calcium and magnesium decreased almost to the vanishing point, and the alkalinity remained almost constant. These phenomena are fully explained by reactions (5) to (9) of Example (2). In the anode compartment, the pH decreased slightly and the alkalinity decreased to about 1/6 its original value. These changes may be explained by the plating out of bicarbonate on some

7. J.A.W.W.A., Vol. 46, 1954, p. 1.

anodic areas in a reaction similar to (1) of Example 2 concurrently with the solution of ferrous iron, reaction (2) of Example 2, at other spots. Unfortunately, the dissolved oxygen changes and ferrous iron concentration changes were not reported.

Some speculation is now in order about what takes place in the corrective treatment of water by means of the calcium carbonate equilibrium. The conventional treatment is to use alkali to slightly supersaturate the water with calcium carbonate. It is thought that the precipitation of calcium carbonate forms a protective coating on the pipe wall. Why the precipitation of calcium carbonate by an ordinary chemical reaction instead of by a half-cell reaction should form a wall coating instead of a slurry has not been explained.

It is now evident from Example 2 that calcium carbonate films are formed by an electrochemical reaction involving dissolved oxygen. It is apparent, however, that the protection against corrosion is afforded by the anodic reaction and not the calcium carbonate film. The important feature is the high pH which prevents the solution of ferrous iron and results in the plating out of carbonate or hydroxide at the anode. As further evidence of this point, iron or steel in contact with strong solutions of sodium carbonate or sodium hydroxide do not corrode. The effectiveness of cement lining in protecting iron pipe from corrosion may be explained by the fact that the pH in the pore water adjacent to the metal is about 12.4 in newly-lined pipe.

Polarization Tests

A piece of corroding metal may be described as an aggregation of numerous small corrosion cells, each with an anodic and cathodic area. If a separate electrode electrically connected to the piece of metal is immersed in the electrolyte and a current made to flow between the separate electrode and the piece of metal by means of an impressed electromotive force, the so-called local or corrosion current on the piece of metal may be modified. This change in the magnitude of the corrosion current is known as polarization. Many investigations have been made in an effort to determine the relation between the polarizing current and the local corrosion current. If the separate electrode is made an anode, the polarizing current may be increased to a point where there is no flow of local corrosion current and the entire piece of metal is cathodic. Such a current is here designated an "anode polarizing current" because it polarizes the anodic areas of the specimen. It is also referred to in the literature as a "cathodic protection current" because it is the type of current used in cathodic protection of submerged metals. Similarly, if the external electrode is made a cathode, the current may be increased in the reverse direction to a point where there is no flow of corrosion current and the entire piece of metal is anodic. Such a current is here designated a "cathode polarizing current." The amount of polarizing current required to produce these results is of particular importance in indicating the current density required for cathodic protection of submerged metals.

Ingenious "null" methods have been devised for measuring the potential between the electrolyte and the corroding metal which automatically eliminate the IR drop of the polarizing current through the electrolyte.⁸ The potential thus measured reflects the increased IR drop through the cathodic films of the test specimen for an anode polarizing current and the increased

8. Pearson, J. M., "Null Methods Applied to Corrosion Measurements," Trans. The American Electrochemical Society, Vol. 81, 1942, p. 485.

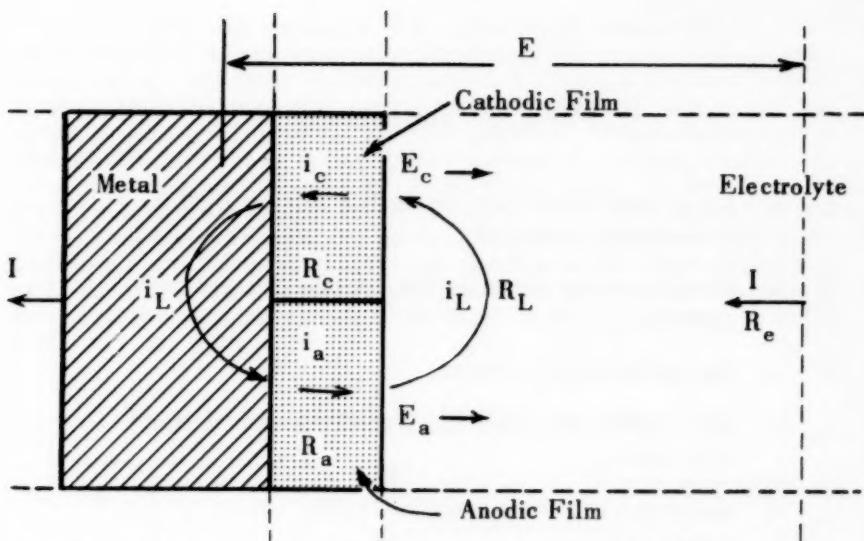


Fig. 4. Polarization of Elementary Corrosion Cell with Anode Polarizing Current.

IR drop through the anodic films of the specimen for a cathode polarizing current. Plots of these potential measurements against corresponding polarizing currents are known as polarization curves.

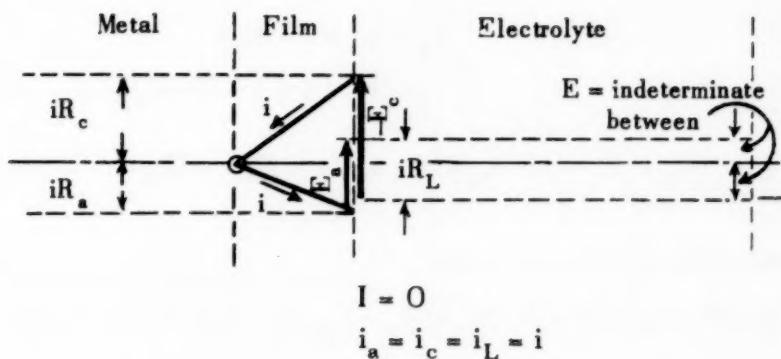
Fig. 4 shows diagrammatically the direction of the current flow in the polarization of an elementary corrosion cell with an anode polarizing current. The figure shows the local current as modified by the polarizing current with the corresponding resistance through the electrolyte, the total current through the cathodic film with the corresponding resistance of the cathodic film, the total current through the anodic film with the corresponding resistance through the anodic film, the resistance of the electrolyte to the polarizing current I , and the electromotive forces of the anodic area and the cathodic area. The resistance through the metal itself to both the local current and the polarizing current is infinitesimally small as compared to the resistance through the films and the electrolyte and has therefore been assumed equal to zero in order to simplify the mathematical development. The total potential between a selected point in the electrolyte and the test metal for a current flowing between the test specimen and the separate electrode (not shown in the figure) is designated in the figure as E . The potential which is measured by the null methods is $E - IR_e$. Although Fig. 4 pictures only a single elementary corrosion cell, it may be considered as representing an entire test specimen where all the anodic areas are grouped into a single area and all the cathodic areas are grouped into a single area. Measurements made with such a test specimen would result in average values for all the elementary cells comprising this specimen.

In order to develop the mathematical theory, the following nomenclature has been used.

Table of Nomenclature

- i = local corrosion current in the absence of a polarizing current I ,
- i_L = local current as modified by the polarizing current I ,
- I = the polarizing current,
- i_a = the current through the anodic areas of the specimen,
- i_c = the current through the cathodic areas of the specimen,
- R_e = the resistance of the electrolyte to the polarizing current I ,
- R_L = the resistance of the electrolyte to the local current i_L ,
- R_a = the resistance of the anodic areas of the specimen to the current i_a ,
- R_c = the resistance of the cathodic areas of the specimen to the current i_c ,
- K_a = the fraction of an anode polarizing current I by which the local corrosion current i is reduced at the anodic areas,
- K_c = the fraction of a cathode polarizing current I by which the local corrosion current i is increased at the anodic areas,
- I_a = the anode polarizing current just sufficient to reduce the current through the anodic areas, i_a , to zero.
- I_c = the cathode polarizing current just sufficient to reduce the current through the cathodic areas, i_c , to zero.

In order to develop the theory, it is necessary to assume that all the resistances and the single electrode potentials, E_a and E_c , remain constant during testing. The local corrosion current, i , also is assumed to remain constant, since the value of i is one of the unknowns to be determined. As will be shown later, K_a and K_c , are also constants. The conditions during testing must therefore be such that the thickness of the films, the temperature and the composition of the electrolyte in the anodic and cathodic areas are not substantially changed during the current flow. The initial film thicknesses should be substantial, the electrolyte should be replaced or mixed continuously and the duration of the test should be short. It is obvious that experiments starting with clean metal specimens will not conform to the above requirements and will yield results which are very difficult to interpret.



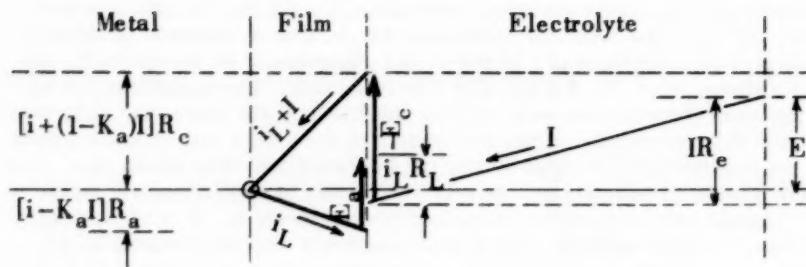
$$E_a - E_c = i(R_a + R_L + R_c) \quad (7)$$

From which $i = \frac{E_a - E_c}{R_a + R_L + R_c}$

External potential to metal,
 E = indeterminate between
 $-E_c + iR_c$ and $E_a - iR_a$

Fig. 5. Analysis of Local Corrosion Cells with Zero Polarizing Current.

Fig. 5 shows an analysis of a local corrosion cell with no polarizing current. The potential drops around the corrosion circuit are shown diagrammatically at the top of the figure together with the relations between the various currents. The application of Kirchhoff's second law is shown in Equation (7) from which the local corrosion current may be evaluated in terms of the



$$I > 0 < I_a$$

$$i_a = i_L = i - K_a I$$

$$i_c = i_L + I = i + (1 - K_a) I$$

$$E_a - E_c = (i - K_a I)(R_a + R_L + R_c) + IR_c \quad (8)$$

External potential to metal,

$$E - IR_e = E_c + [i + (1 - K_a) I] R_c = E_a - (i - K_a I)(R_a + R_L) \quad (9)$$

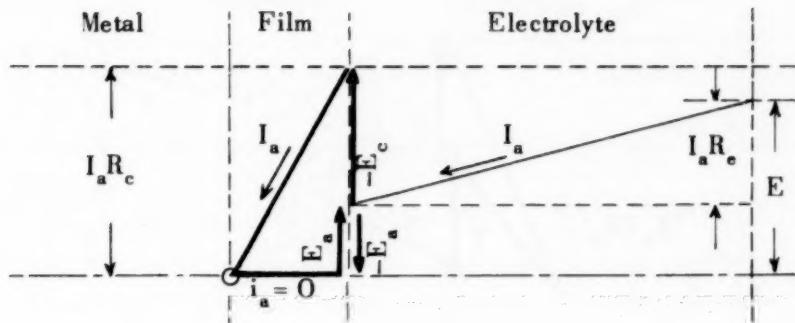
Fig. 6. Analysis of Local Corrosion Cells with Anode Polarizing Current less than I_a .

electromotive force of the cell and the resistances of the circuit. It may be seen from the figure that the external potential to the metal is indeterminate.

Fig. 6 shows diagrammatically the potential drops around the corrosion circuit when the specimen is being subjected to an anode polarizing current of insufficient magnitude to stop the local current flow through the anode. Equation (8) is the application of Kirchhoff's second law for the corrosion circuit, and Equation (9) is for the external potential to the metal.

Fig. 7 shows the potential drops around the corrosion circuit with an anode polarizing current just sufficient to stop the flow of current through the anode. Equation (10) is the application of Kirchhoff's second law to this condition, and Equation (11) is the expression for the external potential to the metal. It will be noted in the figure that the anode potential is just on the point of reversing in direction for this case.

Fig. 8 represents the potential drops through the specimen with an anode polarizing current in excess of that required to stop the flow of current through the anode. In this case, the entire specimen is cathodic. It is probable that the half-cell reaction which occurred at the anode while it was still anodic will not now take place with the reversal of direction because other reactions are more cathodic. Hence, in the figure a different potential has been shown for the cathodic reaction on the areas which previously were anodic.



$$I > 0 = I_a$$

$$i_a = i_L = 0$$

$$i_c = I_a \quad i = K_a I_a$$

$$E_a - E_c = I_a R_c \quad (10)$$

External potential to metal,

$$E - I_a R_e = E_c + I_a R_c = E_a \quad (11)$$

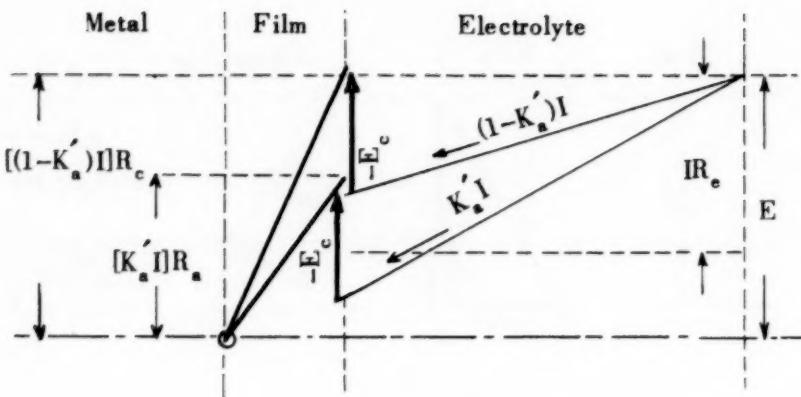
Fig. 7. Analysis of Local Corrosion Cells with Anode Polarizing Current equal to I_a .

Fig. 9 shows diagrammatically the potential drops for the corrosion circuit subjected to a cathode polarizing current of a magnitude insufficient to stop the flow of current through the cathodic areas of the specimen. Equation (12) is the application of Kirchhoff's second law to the corrosion circuit, and Equation (13) is the expression for the external potential to the metal.

Fig. 10 shows diagrammatically the potential drops around the corrosion circuit for a specimen subjected to a cathode polarizing current just sufficient to stop the flow of current through the cathodic areas. Equation (14) is the application of Kirchhoff's second law to the corrosion circuit, and Equation (15) is the expression for the external potential to the metal.

Fig. 11 shows diagrammatically the potential drops corresponding to a cathode polarizing current sufficient to reverse the direction of current flow through the cathodic areas of the specimen. In the figure, the same cathode reaction is shown in reverse which would correspond to the solution of the film previously formed on the cathodic areas. If other reactions would produce a greater potential on the cathode areas, they will supersede the ones which previously took place.

The values of E_a and E_c should be computed before the start of the polarization tests by the methods previously illustrated. During the tests I_a may



$$I > 0 > I_a$$

$$i_L = 0$$

$$-i_a = K'_a I$$

$$i_c = (1-K'_a) I$$

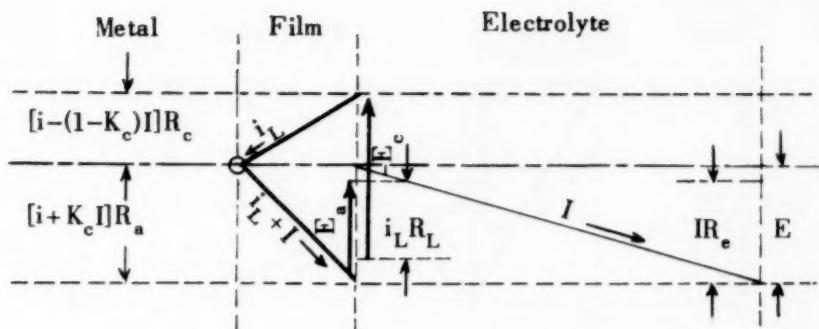
Entire specimen becomes cathodic. E_a is replaced by $-E_c$ on previously anodic areas. Current I is divided with different IR drops through R_a and R_c . Discontinuity in polarization curve to be expected as I exceeds I_a .

Fig. 8. Analysis of Local Corrosion Cells with Anode Polarizing Current greater than I_a .

be evaluated by noting the anode polarizing current when the external potential to the metal equals E_a , as shown by Equation (11). Similarly, I_c may be evaluated by noting the cathode polarizing current when the external potential to the metal equals E_c , as shown by Equation (15). If, however, R_a is zero as will probably be the case at low pH values, the external potential to the metal is constant and equal to E_a with cathode polarizing currents up to the magnitude of I_c ; as may be seen from Equation (13), R_c and R_a may now be evaluated by means of Equation (10) and (14). When the tests are completed and the polarization curves plotted, other unknowns may be evaluated from the curves.

If Equation (7) is subtracted from Equation (8), K_a may be expressed in terms of the resistances as follows:

$$K_a = \frac{R_c}{R_a + R_L + R_c} \quad (16)$$



$$I < 0$$

$$i_c = i_L = i - (1 - K_c)I$$

$$i_a = i_L + I = i + K_c I$$

$$E_a - E_c = (i + K_c I)(R_a + R_L + R_c) - I(R_L + R_c) \quad (12)$$

External potential to metal,

$$E - IR_e = E_c + [i - (1 - K_c)I](R_L + R_c) = E_a - (i + K_c I)R_a \quad (13)$$

Fig. 9. Analysis of Local Corrosion Cells with Cathode Polarizing Current less than I_c .

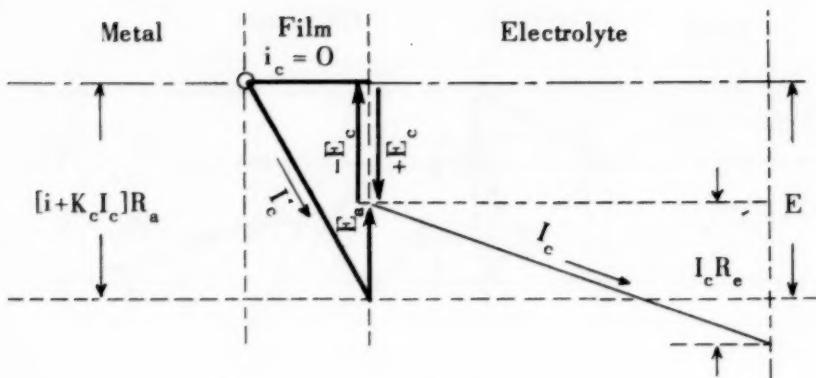
It follows therefore that if the resistances remain constant during the tests, K_a is constant for values of the anode polarizing current up to I_a .

K_a may not be computed directly from Equation (16) because the value of R_L is not yet known. K_a may, however, be evaluated from the experimental data for any two points on the anode polarization curve for values of I less than I_a . If Equation (9) is solved for i in terms of R_c for the data from any two points and the two values of i are equated, the following relation results:

$$K_a = 1 - \frac{(E - IR_e)_2 - (E - IR_e)_1}{(I_2 - I_1)R_c} \quad (17)$$

where $(E - IR_e)_2$ and $(E - IR_e)_1$ are the external potentials to the metal for points 2 and 1 respectively on the anode polarization curve, and I_2 and I_1 are the corresponding anode polarizing currents, both being less than I_a .

If the value of K_a , computed by means of Equation (17), is inserted in Equation (16), with the already known values of R_a and R_c , R_L may be evaluated.



$$I < 0 = I_c$$

$$i_c = i_L = 0$$

$$i_a = I_c, i = (1 - K_c) I_c$$

$$E_a - E_c = I_c R_a \quad (14)$$

External potential to metal,

$$E - I_c R_e = E_c = E_a - I_c R_a \quad (15)$$

Fig. 10. Analysis of Local Corrosion Cells with Cathode Polarizing Current equal to I_c .

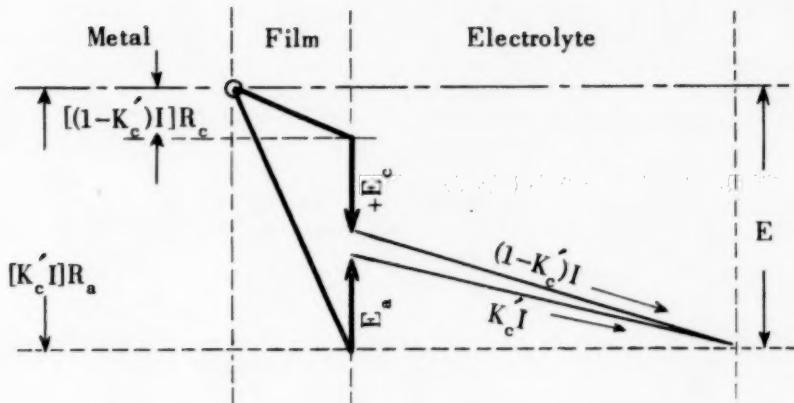
i may now be evaluated from Equation (7) or from any point on the anode polarization curve by means of Equation (9).

If Equation (7) is subtracted from Equation (12), K_c may be expressed in terms of the resistances as follows:

$$K_c = \frac{R_c + R_L}{R_a + R_L + R_c} \quad (18)$$

A comparison of this equation with Equation (16) will show that K_a and K_c are not equal. The assumption that K_a equals K_c which has been made in many previous investigations⁹ involves the complete neglect of R_L . The

9. Muller, W. J., "The Effect of Cathodic Reactions on the Corrosion of Metals from the Viewpoint of the Local Cell Theory," Trans. Electrochemical Soc., Vol. 76, 1939, p. 167; also Pearson, J. M., "Null Methods Applied to Corrosion Measurements," Trans. Electrochemical Soc., Vol. 81, 1942,



$$I < 0 < I_c$$

$$i_a = K'_c I$$

$$-i_c = (1 - K'_c) I$$

Entire specimen becomes anodic. $-E_c$ is changed to an anodic potential corresponding to the possible reactions with highest potential over the cathodic film previously formed. The potential may be $+E_c$ if no other reaction is possible until the film is dissolved. Current I is divided with different IR drops through R_a and R_c . Discontinuity in polarization curve to be expected as I exceeds I_c .

Fig. 11. Analysis of Local Corrosion Cells with Cathode Polarizing Current greater than I_c .

equation

$$i = \frac{I_a I_c}{I_a + I_c}$$

used by these investigators follows directly from the erroneous assumption that K_a equals K_c .

p. 485; also Johnson, P. A. and Babb, A. L., "Thermodynamics of Irreversible Processes Applied to Corrosion," Ind. and Eng. Chemistry, March, 1954, p. 518.

K_c may be computed directly from Equation (18), since all resistances are now known. However, as a check, K_c may also be evaluated from the experimental data for any two points on the cathode polarization curve for values of I less than I_c . If Equation (13) is solved for i in terms of R_c for the data from any two points and the two values of i are equated, the following relation results:

$$K_c = 1 - \frac{(E - IR_e)_1 - (E - IR_e)_2}{(I_2 - I_1)(R_L + R_e)} \quad (19)$$

where the nomenclature is the same as for Equation (17) except that the data are for points on the cathode polarization curve.

Now, if R_a is zero and the external potential to the metal is constant, as has been demonstrated above, $K_c = 1$ from Equation (18) or (19).

A critical examination of Equation (9), which is the equation for the anode polarization curve, will reveal that if the conditions for testing are properly maintained only the polarizing current and external potential to the metal are variables. The equation represents a straight line, and all anode polarization curves should be straight lines. Curvature indicates changes in resistance or composition of electrolyte during testing. Similarly Equation (13) indicates that all cathode polarizing curves should be straight lines. Curvature shows failure to control the conditions of the test as required. K_a and K_c are functions of the slope of the straight line polarization curves.

In order to study the rate of growth and rate of increase in resistance of films, it is desirable to start with clean metal specimens and a constant polarizing current I which is greater in magnitude than I_a for anode polarizing currents and I_c for cathode polarizing currents. The specimen will be all anode for the one case and all cathode for the other case. With the anode polarizing current:

$$E - IR_e = E_c + IR_c \quad (20)$$

and with the cathode polarizing current:

$$E - IR_e = E_a - IR_a \quad (21)$$

Since I is kept constant, the change in external potential to the metal with time is a direct measure of the rate of increase in resistance of the film. Moreover, I , is a measure of the rate of deposit of film. If the composition of the film is previously identified, as it must be to compute the single electrode potential, the rate of deposit by weight may be computed directly from I .

CONCLUSIONS

It is the author's sincere hope that this paper will be studied carefully by all investigators in the corrosion field, so that corrosion research may be placed upon a more scientific basis than is now the case. The principles presented should be examined critically by others both by theoretical analysis and experiment to the end that errors may be found and eliminated.